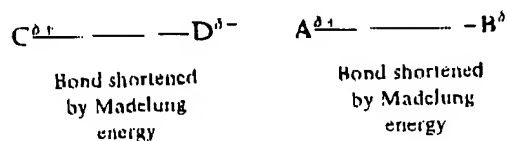Inorganic chemistry, principles of structure and reactivity 3rd. 1983
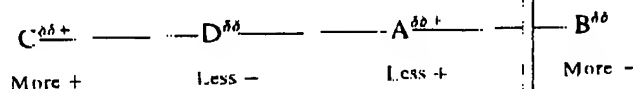
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electron density (see pp. 294–297); thus before interaction, the CDAB system will appear as:

$$C^{\delta+} \text{——} \text{—} D^{\delta-} \qquad A^{\delta+} \text{——} \text{—} B^{\delta}$$

| Bond shortened | Bond shortened |
| by Madelung | by Madelung |
| energy | energy |

The C   D and A   B bonds will be shortened as a result of their polarity (Schomaker-Stevenson Rule). However, upon formation of a D– A bond, the charges will change:

$$C^{\cdot\delta\delta+} \text{——} \text{—} D^{\delta\delta} \text{——} \text{——} A^{\delta\delta+} \text{—} \text{—} B^{\delta\delta}$$

| More + | Less – | Less + | More – |

While there is a net gain in bonding energy in the acid-base region, there is some loss within both the acid molecule and the base molecule, leading to reduction in Madelung energy and Schomaker-Stevenson shortening in these bonds; hence the lengthening of *Rule 1*.


## HARD AND SOFT ACIDS AND BASES

For some time coordination chemists have been aware of certain trends in the stability of metal complexes. One of the earliest correlations was the *Irving-Williams series of stability*.[35] For a given ligand, the stability of complexes with dipositive metal ions follows the order: $Ba^{+2} < Sr^{+2} < Ca^{+2} < Mg^{+2} < Mn^{+} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$. This order arises in part from a decrease in size across the series and in part from ligand field effects (Chapter 9). A second observation is that certain ligands form their most stable complexes with metal ions such as $Ag^{+}$, $Hg^{+2}$, and $Pt^{+2}$, but other ligands seem to prefer ions such as $Al^{+3}$, $Ti^{+4}$, and $Co^{+3}$.[36] Ligands and metal ions were classified[37] as belonging to type (*a*) or (*b*)[38] according to their preferential bonding. Class (*a*) metal ions include those of alkali metals, alkaline earth metals, and lighter transition metals in higher oxidation states such as $Ti^{+4}$, $Cr^{+3}$, $Fe^{+3}$, $Co^{+3}$ and the hydrogen ion, $H^{+}$. Class (*b*) metal ions include those of the heavier transition metals, and those in lower oxidation states such as $Cu^{+}$, $Ag^{+}$, $Hg^{+}$, $Hg^{+2}$, $Pd^{+2}$, and $Pt^{+2}$.[39] According to their preferences toward either class (*a*) or class (*b*) metal ions, ligands may be classified as

[35] H. Irving and R. J. P Williams, *Nature*, 1948, *162*, 746; *J. Chem. Soc.*, 1953, 3192.

[36] The existence of isolated ions of high charge such as $Ti^{+4}$ in chemical systems is energetically unfavorable. Nevertheless, complexes exist with these elements in high formal oxidation states.

[37] S. Ahrland, J. Chatt, and N. R Davies, *Quart. Rev. Chem. Soc.*, 1958, *12*, 265. See also G. Schwarzenbach, *Experientia Suppl.*, 1956, *5*, 162.

[38] The (*a*) and (*b*) symbolism is arbitrary and should not be confused with the A and B subgroups of the periodic table

[39] Only a limited selection of examples of class (*a*) and (*b*) metal ions is given here for the purpose of illustration. A complete listing is provided in Tables 7.8 and 7

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type (a) or (b), respectively. Stability of these complexes may be summarized as follows:

| Tendency to complex with class (a) metal ions | Tendency to complex with class (b) metal ions |
|---|---|
| N >> P > As > Sb | N << P > As > Sb |
| O >> S > Se > Te | O << S < Se ~ Te |
| F > Cl > Br > I | F < Cl < Br < I |

For example, phosphines ($R_3P$) and thioethers ($R_2S$) have a much greater tendency to coordinate with $Hg^{+2}$, $Pd^{+2}$, and $Pt^{+2}$, but ammonia, amines ($R_3N$), water, and fluoride ion prefer $Be^{+2}$, $Ti^{+4}$, and $Co^{+3}$. Such a classification has proved very useful in accounting for and predicting the stability of coordination compounds.

Pearson[40] has suggested the terms "hard" and "soft" to describe the members of class (a) and (b). Thus a hard acid is a type (a) metal ion and a hard base is a ligand such as ammonia or the fluoride ion. Conversely, a soft acid is a type (b) metal ion and a soft base is a ligand such as a phosphine or the iodide ion. A thorough discussion of the factors operating in hard and soft interactions will be postponed temporarily, but it may be noted now that the hard species, both acids and bases, tend to be small, slightly polarizable species and that soft acids and bases tend to be larger and more polarizable. Pearson has suggested a simple rule (sometimes called Pearson's principle) for predicting the stability of complexes formed between acids and bases: *Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases*. It should be noted that this statement is not an explanation or a theory, but a simple rule of thumb which enables the user to predict qualitatively the relative stability of acid–base adducts.

### Classification of acids and bases as hard or soft

In addition to the (a) and (b) species discussed above that provide the nucleus for a set of hard and soft acids and bases, it is possible to classify any given acid or base as hard or soft by its apparent preference for hard or soft reactants. For example, a given base, **B**, may be classified as hard or soft by the behavior of the following equilibrium:[41]

$$BH^+ + CH_3Hg^+ \rightleftharpoons CH_3HgB^+ + H^+ \tag{7.60}$$
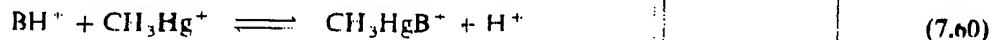
In this competition between a hard acid ($H^+$) and a soft acid ($CH_3Hg^+$), a hard base will cause the reaction to go to the left, but a soft base will cause the reaction to proceed to

[40] R. G. Pearson. *J. Am. Chem. Soc.*, 1963, 85, 3533. Recent summaries have been provided by Pearson [*J. Chem. Educ.*, 1968, 45, 581, 643: *Surv. Progr. Chem.*, 1969, 1, 1, A. Scott ed., Academic Press, New York.] For further reading on this topic, see *Struc. Bonding*, 1966, 1, C. K. Jørgensen et al., which contains papers from a symposium on this subject. For the interesting application to organic chemistry, see R. G. Pearson and J Songstad, *J. Am. Chem. Soc.*, 1967, 89, 1827, and T-L. Ho, *Chem. Rev.*, 1975, 75, 1, and "Hard and Soft Acids and Bases Principle in Organic Chemistry," Academic Press, New York, 1977.

[41] If this equilibrium is studied in aqueous solution as is usually the case, all species will be hydrated, and, specifically, the acids will occur as $CH_3Hg(H_2O)^+$ and $H_3O^+$. For data on equilibria of this type, see G. Schwarzenbach and M Schellenberg. *Helv. Chim. Acta*, 1965, 48, 28

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**Table 7.8** Classification of hard and soft acids

*Hard acids*

$H^+$, $Li^+$, $Na^+$, $K^+$ ($Rb^+$, $Cs^+$)
$Be^{+2}$, $Be(CH_3)_2$, $Mg^{+2}$, $Ca^{+2}$, $Sr^{+2}(Ba^{+2})$
$Sc^{+3}$, $La^{+3}$, $Ce^{+4}$, $Gd^{+3}$, $Lu^{+3}$, $Th^{+4}$, $U^{+4}$, $UO_2^{+2}$, $Pu^{+4}$
$Ti^{+4}$, $Zr^{+4}$, $Hf^{+4}$, $VO^{+2}$, $Cr^{+3}$, $Cr^{+6}$, $MoO^{+3}$, $WO^{+4}$, $Mn^{+2}$, $Mn^{+7}$, $Fe^{+3}$, $Co^{+3}$
$BF_3$, $BCl_3$, $B(OR)_3$, $Al^{+3}$, $Al(CH_3)_3$, $AlCl_3$, $AlH_3$, $Ga^{+3}$, $In^{+3}$
$CO_2$, $RCO^+$, $NC^+$, $Si^{+4}$, $Sn^{+4}$, $CH_3Sn^{+3}$, $(CH_3)_2Sn^{+2}$
$N^{+3}$, $RPO_2^+$, $ROPO_2^+$, $As^{+3}$
$SO_3$, $RSO_2^+$, $ROSO_2^+$
$Cl^{+3}$, $Cl^{+7}$, $I^{+5}$, $I^{+7}$
HX (hydrogen-bonding molecules)

*Borderline acids*

$Fe^{+2}$, $Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Zn^{+2}$
$Rh^{+3}$, $Ir^{+3}$, $Ru^{+3}$, $Os^{+2}$
$B(CH_3)_3$, $GaH_3$
$R_3C^+$, $C_6H_3^+$, $Sn^{+2}$, $Pb^{+2}$
$NO^+$, $Sb^{+3}$, $Bi^{+3}$
$SO_2$

*Soft acids*

$Co(CN)_3^{-3}$, $Pd^{+2}$, $Pt^{+2}$, $Pt^{+4}$
$Cu^+$, $Ag^+$, $Au^+$, $Cd^{+2}$, $Hg^+$, $Hg^{+2}$, $CH_3Hg^+$
$BH_3$, $Ga(CH_3)_3$, $GaCl_3$, $GaBr_3$, $GaI_3$, $Tl^+$, $Tl(CH_3)_3$
$CH_2$, carbenes
Pi-acceptors: trinitrobenzene, chloranil, quinones, tetracyanoethylene, etc.
$HO^+$, $RO^+$, $RS^+$, $RSe^+$, $Te^{+4}$, $RTe^+$
$Br_2$, $Br^+$, $I_2$, $I^+$, ICN, etc.
O, Cl, Br, I, N, $RO·$, $RO_2·$
$M^0$ (metal atoms) and bulk metals

the right.[42] The methylmercury cation is convenient to use because it is a typical soft acid and, being monovalent like the proton, simplifies the treatment of the equilibria. Complete listings of hard and soft acids and bases are given in Tables 7.8 and 7.9.

An important point to remember in considering the information in these tables is that the terms hard and soft are relative with no sharp dividing line between them. This is illustrated in part by the third category, "borderline," for both acids and bases. But even within a group of hard or soft, not all will have equivalent hardness or softness. Thus, although all alkali metal ions are hard, the larger, more polarizable cesium ion will be somewhat softer than the lithium ion. Similarly, although nitrogen is usually hard because of its small size, the presence of polarizable substituents can affect its behavior. Pyridine, for example, is sufficiently softer than ammonia to be considered borderline.

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[42] An interesting historical sidelight on this type of soft–soft interaction is the origin of the name "mercaptan," a *mercury capturer*: $Hg^{+2} + 2RSH = Hg(SR)_2 + 2H^+$

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**Table 7.9 Classification of hard and soft bases**

*Hard bases*

$NH_3$, $RNH_2$, $N_2H_4$

$H_2O$, $OH^-$, $O^{2-}$, $ROH$, $RO^-$, $R_2O$

$CH_3COO^-$, $CO_3^{-2}$, $NO_3^-$, $PO_4^{3-}$, $SO_4^{-2}$, $ClO_4$

$F^-$ $(Cl^-)$

*Borderline bases*

$C_6H_5NH_2$, $C_5H_5N$, $N_3^-$, $N_2$

$NO_2^-$, $SO_3^{-2}$

$Br^-$

*Soft bases*

$H^-$

$R^-$, $C_2H_4$, $C_6H_6$, $CN^-$, $RNC$, $CO$

$SCN^-$, $R_3P$, $(RO)_3P$, $R_3As$

$R_2S$, $RSH$, $RS^-$, $S_2O_3^{-2}$
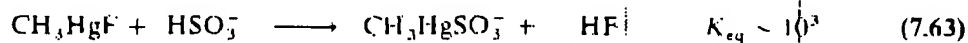
$I^-$

## Acid-base strength and hardness and softness

Hardness and softness refer to special stability of hard–hard and soft–soft interactions and should be carefully distinguished from inherent acid or base strength. For example, both $OH^-$ and $F^-$ are hard bases; yet the basicity of the hydroxide ion is about $10^{13}$ times that of the fluoride ion. Similarly, both $SO_3^{-2}$ and $Et_3P$ may be considered soft bases; however, the latter is $10^7$ times as strong (toward $CH_3Hg^+$). It is possible for a *strong* acid or base to displace a weaker one, even though this *appears* to violate the principle of hard and soft acids and bases. For example, the *stronger, softer* base, the sulfite ion, can displace the *weak, hard base*, fluoride ion, from the *hard acid*, the proton, $H^+$:
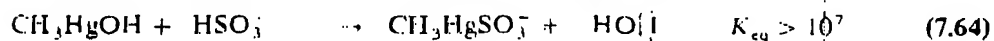
$$SO_3^{2-} + HF \longrightarrow HSO_3^- + F^- \qquad K_{eq} \sim 10^4 \qquad (7.61)$$
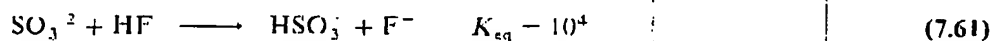
Likewise the *very strong, hard base*, hydroxide ion, can displace the weaker *soft base*, sulfite ion, from the *soft acid*, methylmercury cation:

$$OH^- + CH_3HgSO_3 \longrightarrow CH_3HgOH + SO_3^{2-} \qquad K_{eq} \sim 10 \qquad (7.62)$$
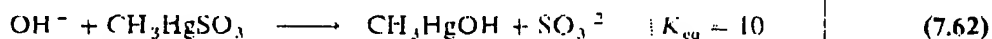
In these cases the *strengths* of the bases ($SO_3^{-2} > F^-$, Eq. 7.61; $OH^- > SO_3^{-2}$, Eq. 7.62), are sufficient to force these reactions to the right in spite of hard–soft considerations. Nevertheless, if a competitive situation is set up in which both strength *and* hardness–softness are considered, the hard–soft rule works:

$$CH_3HgF + HSO_3^- \longrightarrow CH_3HgSO_3^- + HF \qquad K_{eq} \sim 10^3 \qquad (7.63)$$

$\qquad$ Soft–hard $\quad$ Hard-soft $\qquad\qquad$ Soft–soft $\quad$ Hard–hard

$$CH_3HgOH + HSO_3 \longrightarrow CH_3HgSO_3^- + HOH \qquad K_{eq} > 10^7 \qquad (7.64)$$

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**Table 7.10** Basicity toward the proton and methylmercury cation

| Base | Linking atom | $pK_a$ $(CH_3Hg^+)$ | $pK_b$ $(H^+)$ |
|------|--------------|---------------------|----------------|
| F | F | 1.50 | 2.85 |
| Cl | Cl | 5.25 | −7.0 |
| Br | Br | 6.62 | −9.0 |
| I | I | 8.60 | 9.5 |
| OH | O | 9.37 | 15.7 |
| $HPO_4^-$ | O | 5.03 | 6.79 |
| $S^{-2}$ | S | 21.2 | 14.2 |
| $HOC_2H_4S$ | S | 16.12 | 9.52 |
| $SCN^-$ | S | 6.05 | ~4 |
| $SO_3^{-2}$ | S | 8.11 | 6.79 |
| $S_2O_3^{-2}$ | S | 10.90 | negative |
| $NH_3$ | N | 7.60 | 9.42 |
| $NH_2C_6H_4SO_3^-(p)$ | N | 2.60 | 3.06 |
| $\phi_2PC_6H_4SO_3^-$ | P | 9.15 | ~0 |
| $Et_2PC_2H_4OH$ | P | 14.6 | 8.1 |
| $Et_3P$ | P | 15.0 | 8.8 |
| $CN^-$ | C | 14.1 | 9.14 |

$^a pK_s = \log[CH_3HgB] [CH_3Hg^-][B]$.
$^b pK_h = \log[HB] [H^+][B]$.

In considering acid–base interactions, it is necessary to consider both strength *and* hardness–softness. Table 7.10 lists the strengths of various bases toward the proton ($H^+$) and the methylmercury cation ($CH_3Hg^+$). Bases such as the sulfide ion ($S^{-2}$) and triethyl-phosphine ($Et_3P$) are very strong toward both the methylmercury ion and the proton, but about a million times better toward the former; hence they are considered *soft*. The hydroxide ion is a strong base toward both acids, but in this case about a million times better toward the proton: hence it is hard. The fluoride ion. $F^-$, is not a particularly good base toward either acid but slightly better toward the proton as expected from its hard character.

The importances of both inherent acidity and a second hard -soft factor is well shown by the Irving-Williams series and some oxygen, nitrogen, and sulfur chelates (Fig. 7.5). The Irving-Williams series of increasing stability from $Ba^{+2}$ to $Cu^{+2}$ is a measure of increasing inherent acidity of the metal (largely due to decreasing size). Superimposed upon this is a hardness- softness factor in which the softer species coming later in the series (greater number of *d* electrons, see p. 319) favor ligands $S > N > O$. The harder alkaline earth and early transition metals ions (few or no *d* electrons) preferentially bind in the order $O > N > S$.

### Symbiosis

As noted above, the hardness or softness of an acidic or basic site is not an inherent property of the particular atom at that site but can be influenced by the substituent atoms. The addition of soft, polarizable substituents can soften an otherwise hard center and the presence of electron-withdrawing substituents can reduce the softness of a site. The acidic